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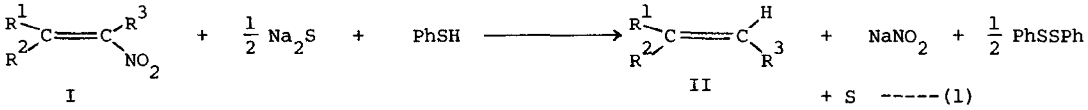
A NEW SYNTHESIS OF OLEFINS. CONVERSION OF NITROOLEFINS INTO OLEFINS BY REDUCTIVE ELIMINATION

Noboru Ono*, Shuji Kawai, Kazuhiko Tanaka and Aritsune Kaji
Department of Chemistry, Faculty of Science, Kyoto University,
Kyoto 606, Japan

Summary; A nitro group in nitroolefins is displaced by hydrogen giving the corresponding olefins in good yields by the reaction of nitroolefins with sodium sulfide in the presence of benzenethiol. It proceeds rapidly at room temperature.

Nitroolefins(I) are easy to synthesize in good yields and have proved to be intermediates for the facile production of ketones, aldehydes, alcohols, amines and oximes.[1)] In this paper we wish to report another new utilization of I in organic synthesis; nitroolefins substituted with a good electron accepting group such as an aromatic ring or a carbonyl group are readily converted into olefins(II)in good yields by the reaction of I with sodium sulfide($Na_2S \cdot 9H_2O$) in the presence of benzenethiol.



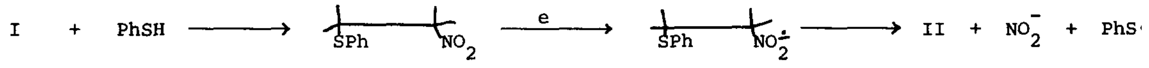
$$R^1R^2C{=}C(R^3)NO_2 + \frac{1}{2}Na_2S + PhSH \longrightarrow R^1R^2C{=}C(H)R^3 + NaNO_2 + \frac{1}{2}PhSSPh + S \quad \text{-----(1)}$$

Reduction of I to II proceeds very rapidly at room temperature and the procedure of the reaction is very simple. For example, a mixture of 2,2-diphenyl-1-nitroethylene(1.35g, 0,006 mol), $Na_2S \cdot 9H_2O$(1.44g, 0.006 mol) and benzenethiol(0.79g, 0.0072 mol) in DMF(18 ml) was stirred at room temperature for 5 min. Working up the reaction mixture in the usual way followed by distillation gave pure diphenylethylene(1.01g, 94% yield); bp 117-118°C/2.5mmHg. Various nitroolefins were reduced to olefins by the present procedure. Results are summarized in the Table 1. The yields in this table refer to pure and isolated products. Purification was done by distillation or recrystallization from ethanol. Every reaction in the table is complete for 2-5 min, so the labile group like a nitro group at an aromatic ring or an ester group can survive under reaction conditions. The presence of benzenethiol is essential for the present reductive elimination, for the yields of olefins are very poor in the absence of benzenethiol or in the presence of phenol as a proton source. We believe the present method should find wide applicability, for the requisite starting materials are readily available. Nitroolefins are easily prepared by condensation of carbonyl compounds and nitroparaffins[2)], the reaction of imines with nitromethane[3)], or phenylation of nitroolefins with benzene using palladium acetate as a catalyst.[4)]

Table 1 Olefins Prepared by the Reaction of I with Sodium Sulfide

R^1	R^2	R^3	Yield(%)	mp(or bp)
C_6H_5	C_6H_5	H	94	(117-118°/2.5mmHg)
C_6H_5	H	C_6H_5	93	123-124°
$4\text{-}Cl\text{-}C_6H_4$	H	C_6H_5	83	132-133°
$4\text{-}CH_3O\text{-}C_6H_4$	H	C_6H_5	86	137-138°
$4\text{-}CH_3\text{-}C_6H_4$	H	C_6H_5	91	118-119°
$2\text{-}Cl\text{-}C_6H_4$	H	C_6H_5	94	37-38°
$3\text{-}NO_2\text{-}C_6H_4$	H	C_6H_5	76	111-112°
$2\text{-}Cl\text{-}C_6H_4$	H	$4\text{-}CH_3\text{-}C_6H_4$	93	37°
$4\text{-}CH_3O\text{-}C_6H_4$	H	$4\text{-}CH_3\text{-}C_6H_4$	88	173°
$4\text{-}Cl\text{-}C_6H_4$	H	$iso\text{-}C_3H_7$	70	(128°/15mmHg)
$4\text{-}Cl\text{-}C_6H_4$	H	C_2H_5	60	(120°/15mmHg)
C_6H_5	H	$COOC_2H_5$	95	(144°/15mmHg)

The reaction mechanism has not been studied thoroughly, but it is plausible that the reaction proceeds through the intermediate of β-nitrosulfide which should be formed by the reaction of I with benzenethiol. Elimination of the nitro and phenylthio group from this intermediate may involve radical anions as shown below.



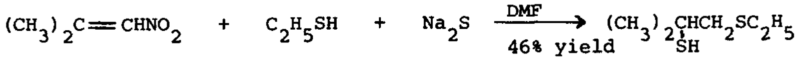
$$2PhS\cdot \longrightarrow PhSSPh$$

If this mechanism is correct, the amounts of sodium sulfide and benzenthiol to complete the reaction are 0.5 mol and 1 mol for 1 mol of nitroolefin, respectively. Table 2 shows that is true, where the results of elimination under various conditions are summarized.

Table 2 Amounts of I, PhSH and Na_2S to Complete the Reaction of eq 1

I(mol)	PhSH(mol)	Na_2S(mol)	Yield of II(%)
1.0	1.2	1.0	93
1.0	1.2	0.5	90
1.0	1.2	0.25	43
1.0	0.6	0.5	51

Unfortunately, the present procedure cannot extend to the purely aliphatic systems, for the side reaction predominates as shown in eq 2. The effort to overcome this difficulty is now in progress.



$$(CH_3)_2C{=}CHNO_2 + C_2H_5SH + Na_2S \xrightarrow[\text{46\% yield}]{\text{DMF}} (CH_3)_2\underset{\displaystyle SH}{C}HCH_2SC_2H_5 \qquad (2)$$

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3) A. Dornow and S. Lüpfert, Chem. Ber., 90, 1780(1957). 4) K. Yamamura and S. Watarai, Bull. Chem. Soc. Jpn., 48, 3757(1975).

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